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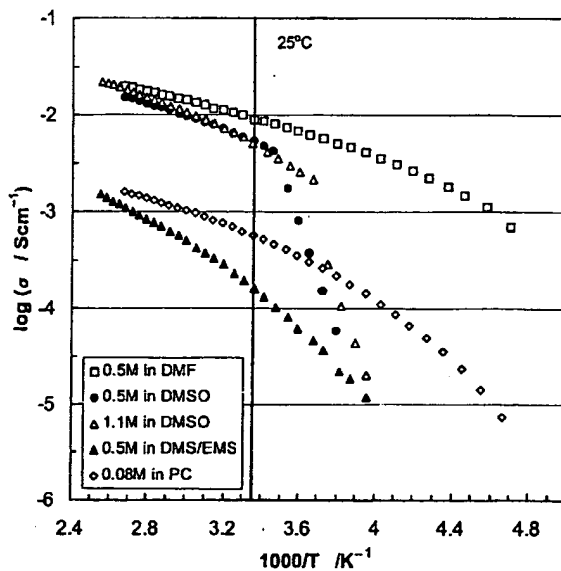
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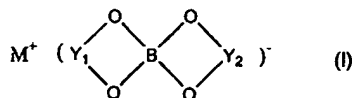
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(54) Title: ELECTROLYTIC SALTS FOR LITHIUM BATTERIES



Ionic conductivities of LiBMB solutions.

(57) Abstract: Orthoborate salts suitable for use as electrolytes in lithium batteries and methods for making the electrolyte salts are provided. The electrolytic salts have one of the formulae (I). In this formula anionic orthoborate groups are capped with two bidentate chelating groups, Y₁ and Y₂. Certain preferred chelating groups are dibasic acid residues, most preferably oxalyl, malonyl and succinyl, disulfonic acid residues, sulfoacetic acid residues and halo-substituted alkenes. The salts are soluble in non-aqueous solvents and polymeric gels and are useful components of lithium batteries in electrochemical devices.





For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

ELECTROLYTIC SALTS FOR LITHIUM BATTERIES

This application claims priority rights based on U.S. Provisional Application Serial No. 60/212,231, filed June 16, 2000 and 60/290,864 filed May 14, 2001. The above-identified provisional applications are hereby incorporated by reference.

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Financial assistance for this project was provided by the U.S. Government through the Department of Energy under Grant Nos. DEFG0393ER14378-003 and DEFG0395ER45541. Therefore, the United States Government may own certain rights to this invention.

10

INTRODUCTION

1. Technical Field

The present invention relates to novel electrolytic salts having high conductivity suitable for use in lithium batteries, especially secondary lithium batteries.

15

2. Background

Lithium batteries supply energy to a growing number of portable electrochemical devices and are a promising energy source for larger applications such as electric automobiles. Accordingly, lithium batteries are the subject of intense research and the effort to improve performance continues.

20

A major area of interest has been in the field of electrolytes for lithium cells where electrolytes with high ionic conductivity, wide electrochemical stability window and good lithium ion transport number have been the goal. Electrolytic solutions are generally prepared by dissolving a highly-conductive salt in a proper non-aqueous solvent or a mixture of several solvents and polymer electrolytes are generally prepared by dissolving a highly-conductive salt in a polymer, usually an ether polymer, to make solid polymeric electrolytes (SPE). Examples of suitable electrolytes have been disclosed in US Patent No. 5,849,432, US Patent No. 5,824,433, US Patent No. 5,660,947.

10 The electrolyte solute lithium hexafluorophosphate (LiPF_6) is currently the electrolytic salt used commercially in lithium batteries (1), but this electrolyte exhibits a thermal instability that restricts its use to ambient temperature (2). Investigations of weakly coordinating anion groups continue to spur the development of new salts suitable for inclusion into electrolytic solutions and SPE (3,4). In the past ten years
15 many novel kinds of electrolytic salts, showing high ionic conductivity, large electrochemical stability and high thermal stability in solutions, have been reported. Howelss et al. disclose substituted imides in US Patent No. 5,874,616. Various chelatoborates have been studied (4.5) and a highly conductive salt, lithium bis(oxalato)borate (LiBOB), has recently been disclosed in DE 19829030. This salt
20 has been further characterized and shows promise as an electrolytic solution in lithium batteries (7). Heide et al. disclose orthoborates as additives in electrolytes for improved performance of electrochemical cells in European Patent Application 1,035,612.

Accordingly, novel electrolytic salts are still being sought.

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BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates DTA trace thermogram at $10^{\circ}\text{C min}^{-1}$ for pure
 $\text{LiB}[\text{OC}(\text{CF}_3)_2]_4$ or LiBPFPB, showing fusion at 120°C and decomposition at 280°C .

20 Figure 2 illustrates ionic conductivities of LiBPFPB and its solutions in 1M
acetonitrile (AN), 0.6M DME, 1M PC and 1M DMS-EMS (15:85 by weight).

Figure 3 illustrates ionic conductivities of 1M LiBOB solutions.

Figure 4 illustrates ionic conductivities of LiBMB solutions.

Figure 5 illustrates temperature dependence of ionic conductivity of a gel electrolyte (Gel #1) with composition of 21.17 PMMA (MW 996,000), 7.88 LiBOB, 35.48 EC and 35.47 PC.

Figure 6 illustrates cyclic voltammograms of LiBPFPB in DME and PC solutions, parts (a) and (b) respectively, in a cell with Pt as working electrode and lithium as counter and reference electrodes. Working electrode area: $4.91 \times 10^{-4} \text{ cm}^2$; Scan rate: 1 mVs^{-1} .

Figure 7 illustrates lithium deposition-stripping process and electrochemical stability of 1M LiBOB-PC solution scanned at 1 mV s^{-1} in the voltage range of (a) $-0.3 \sim 6 \text{ V}$ and (b) $1 \sim 4.5 \text{ V}$ vs. Li^+/Li at room temperature. The area of platinum wire working electrode is $4.91 \times 10^{-4} \text{ cm}^2$. The "window" is at least 4.5 V .

Figure 8 illustrates electrochemical stability of LiBMB solutions in PC (a) and DMSO (b), respectively. Area of platinum working electrode $4.91 \times 10^{-4} \text{ cm}^2$.

SUMMARY OF THE INVENTION

It has been discovered that certain orthoborate salts suitable for use as electrolytes in lithium batteries may be readily prepared. The salts comprise orthoborate anionic groups capped with two bidentate chelating groups. The capping groups may be the same or different. The orthoborate capping groups are preferably certain dibasic acid residues, i.e., diacyl, most preferably oxalyl, malonyl and succinyl. Certain other capping groups comprise disulfonic acid residues and sulfoacetic acid residues. Certain other capping groups comprise halo-substituted alkylenes.

Methods for making the conductive salts are provided. In a preferred method, an alkoxy orthoborate salt and the di(trimethylsilyl) dibasic acid ester of the chelate are provided. The orthoborate salt and the silyl ester are combined to form the capped borate salt. In another preferred method, the acidic chelate is provided and is reacted
5 with boric acid under basic conditions to form the capped borate salt.

The conductivity in non-aqueous solvents, the electrochemical window and thermal stability of the present orthoborate salts make them excellent electrolytes for electrochemical devices. The electrolytic salts have been incorporated into conductive gels suitable for use in lithium batteries, especially secondary lithium
10 batteries.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The tetragonally coordinated orthoborate anion is a weak Lewis base that provides four oxygen atoms for binding to suitable ligands. The choice of ligand
15 determines the bonding strength of the Lewis base for its counter ion. It has been discovered that highly conductive electrolytes may be prepared by capping the orthoborate anion with certain electron withdrawing ligands that delocalize the electron density of the orthoborate anion. The capping ligands form stable bonds to the orthoborate and stable salts with good electrochemical window and stability above
20 ambient temperature result.

The salts comprise orthoborate anionic groups capped with two bidentate chelating groups. In certain instances, the capping groups are the same. In certain other instances, the capping groups are different. The orthoborate capping groups are preferably bidentate chelates that bind pairwise – i.e., each chelate comprises two

reactive groups and each reactive group binds an oxygen of the tetragonal orthoborate anion. Preferred capping groups are from dicarboxylic acids and R-substituted dicarboxylic acids, most preferably oxalic acid, malonic acid and succinic acid.

Certain other preferred capping groups comprise disulfonic acid, R-substituted

- 5 disulfonic acid, sulfoacetic acid, and R substituted sulfoacetic acid, preferably fluoro-substituted sulfoacetic acid wherein R is preferrably hydrogen, alkyl or halo.

In certain other instances the capping group may be a halo-substituted alkylene,

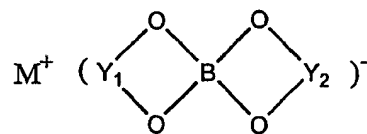
preferably lithium bis(tetrafluoroethylenediolato)borate $\text{LiB}(\text{OCF}_2\text{CF}_2\text{O})_2$,

lithium bis(hexafluoropropylenediolato)borate $\text{LiB}[\text{OCF}(\text{CF}_3)\text{CF}_2\text{O}]_2$ and

- 10 lithium bis[1,2-tetrakis(trifluoromethyl)ethylenediolato(2-),O,O']borate or lithium bis(perfluoropinacolato)borate $\text{LiB}[\text{OC}(\text{CF}_3)_2\text{C}(\text{CF}_3)_2\text{O}]_2$ or $\text{LiB}[\text{OC}(\text{CF}_3)_2]_4$ or

LiBPFPB . The perfluoropinacolato salt was disclosed by Xu, W. and Angell, C. A. in *Electrochemical and Solid-State Letters*, 3(8), 366-368 (2000) and is herein incorporated by reference.

- 15 The electrolyte salts of the present invention have one of the formulae:



- Y_1 and Y_2 are each bound to a pair of said oxygens and are selected from the group comprising $\text{XC}-(\text{CR}_2)_a\text{CX}$ wherein a is 0 to 4 and X is $=\text{O}$, $-\text{C}=\text{N}$, CR'_3 or R'_3 wherein R' is halo, R is hydrogen, alkyl, cyano, or halo provided that
- 20 when a is 0 and X is CF_3 or $=\text{O}$, Y_1 is not Y_2 ; and, $\text{O}_2\text{S}(\text{CR}_2)_b\text{SO}_2$ and $\text{OC}(\text{CR}_2)_b\text{SO}_2$ wherein b is 1 to 4 and R is hydrogen, alkyl, or halo, wherein Y_1 and Y_2 are the same or different in each occurrence;

M^+ is a metal ion selected from the Group I or Group II elements, preferably from Group I and most preferably lithium.

In an important aspect of the present invention, methods for preparing the electrolytic salts are presented. In a preferred method, an alkoxy orthoborate salt, preferably
5 lithium tetramethanolatoborate and the di(trimethylsilyl) ester of the chelate are provided. Thus, for example, when the bis(oxalato)borate salt is desired, di(trimethylsilyl) oxalate is provided. When bis(methylenedisulfonato)borate salt is desired, di(trimethylsilyl)methylenedisulfonate is provided. When mixed capping groups are desired, as in the (oxalatomalonato)borate salt, a mixture of
10 di(trimethylsilyl) malonate and di(trimethylsilyl) oxalate are provided. All these salts may be prepared by methods known in the art as described in the following examples.

In another preferred method, the acid form of the capping group is combined with boric acid and a metal base and allowed to react to form the capped orthoborate salt. In this method, the metal is preferably to be a metal chosen from the Group I
15 group of elements, most preferably lithium. Thus, for example, when an orthoborate salt comprising the capping groups malonyl is desired, (e.g., lithium bis(malonato)borate), double molar amounts of malonic acid and mono molar amount of, boric acid and lithium hydroxide are combined and caused to react. When an orthoborate salt comprising different capping groups is desired, e.g., lithium
20 (malonatooxalato) borate, equal molar amounts of malonic acid, oxalic acid, boric acid and lithium hydroxide are provided. When an orthoborate salt comprising the capping groups sulfoacetyl is desired, double molar amounts of sulfoacetic acid, and mono molar amount of boric acid and lithium hydroxide are provided.

In another aspect of the present invention, conductive electrolytic solutions of the lithium orthoborate salts are provided. Preferred non-aqueous solvents are carbonate or non-carbonate plasticizers or their mixtures. Suitable carbonate plasticizers are, for example, ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). Suitable non-carbonate plasticizers are 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), dimethylsulfoxide (DMSO), dimethyl sulfone (DMS), ethylmethylsulfone (EMS), γ -butyrolactone (BL). Preferred plasticizer mixtures are EC-PC, EC-DMC, EC-DMC-DEC, and PC-DME. The conductivities of certain preferred embodiments of the present invention in the presence of certain of these plasticizers are given in Figures 2,3 and 4.

In yet another aspect of the present invention, gel electrolytes comprising certain embodiments of the present salts are given. A salt is dissolved in a solvent as disclosed hereinabove and the solution is added to a high molecular weight polymer. Suitable polymers are those polymers, poly(methyl methacrylate, (PMMA), or polyacrylonitrile, (PAN) for example, that are generally used in solid polymeric electrolyte (SPE) for electrochemical applications.

An important aspect of the present invention presents the battery performance of the orthoborate electrolytes of the present invention. Batteries comprising a lithium anode and a composite cathode membrane with certain electrolytic salts of the present invention exhibit good performance and multiple galvanostatic charge-discharge cyclic curves.

These and other features, aspects and advantages of the present invention will become better understood with reference to the following descriptive examples.

EXAMPLE 1

This example illustrates the synthesis of a lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two oxalyl groups, to give an anion of bis(oxalato)borate. This compound has a formula lithium bis(oxalato)borate, LiBOB. The preparation included the following three steps.

(1) Lithium tetramethanolatoborate, $\text{LiB}(\text{OCH}_3)_4$, was synthesized following the procedures described by Barthel *et al.* (J. Barthel, R. Buestrich, E. Carl and H. J. Gores, *J. Electrochem. Soc.*, **143**, 3572 (1996).) The yield was 95%. NMR spectra in $\text{DMSO}-d_6$: ^1H , δ 3.16ppm (s); ^{13}C , δ 48.56ppm; ^7Li (referenced to LiNO_3 in D_2O), δ 1.05ppm; and ^{11}B (referenced to $\text{BF}_3\cdot\text{Et}_2\text{O}$ in CDCl_3), δ 7.84ppm.

(2) Di(trimethylsilyl) oxalate, DTMSO, was synthesized according to the method by Hergott and Simchen (H. H. Hergott and G. Simchen, *Synthesis*, 626 (1980).), by reacting 0.20 mol oxalic acid and 0.46 mol chlorotrimethylsilane in anhydrous 1,2-dichloroethane at around 70°C till all acid had reacted (about 3 days). After evaporating the low boiling point solvent and unreacted chlorotrimethylsilane, the residual was distilled under high vacuum. The colorless fraction of b.p. 65-68°C/0.5mmHg was collected, which crystallized quickly on cooling. The yield was 71%. NMR spectra in CDCl_3 : ^1H , δ 0.36ppm (s); ^{13}C , δ 158.31 and -0.51ppm; and ^{29}Si (referenced to TMS in CDCl_3), δ 7.42ppm.

(3) LiBOB was obtained by stirring 0.025 mol lithium tetramethanolatoborate, $\text{LiB}(\text{OCH}_3)_4$, and 0.050 mol di(trimethylsilyl) oxalate (DTMSO) in a large amount of anhydrous acetonitrile (AN) in an oil bath at 45-50°C overnight. The white solid $\text{LiB}(\text{OCH}_3)_4$ disappeared and the solution became slightly cloudy. After rotary-evaporating all low boiling point compounds

(methoxytrimethylsilane formed according to scheme 1, and solvent (AN
acetonitrile) at a temperature below 50°C under reduced pressure, the crude solid
product was dried in an oven at 75°C under high vacuum for 24 hours. LiBOB was
then recrystallized from boiling acetonitrile/toluene (1:1 mixture), subsequent cooled
5 to -20°C. After filtration, the product was dried in a vacuum oven at 80°C for 48
hours to give a white solid, in high yield, around 92%. NMR spectra in DMSO-*d*₆: ¹H,
only for solvent; ¹³C, δ 158.10ppm; ⁷Li (referenced to LiNO₃ in D₂O), δ 0.98ppm; and
¹¹B (referenced to BF₃·Et₂O in CDCl₃), δ 12.20ppm. Elemental analysis for C: found
24.68%, calculate (for C₄O₈BLi) 24.74%.

10 Example 2

This example illustrates the synthesis of a lithium salt of an orthoborate in
which the four boron oxygens are pairwise connected by two malonyl groups, to give
an anion of bis(malonato)borate. This compound has a formula lithium
bis(malonato)borate, LiBMB. The preparation included the similar three steps in
15 Example 1, just using malonic acid to replace oxalic acid and di(trimethylsilyl)
malonate (DTMSM) to replace di(trimethylsilyl) oxalate (DTMSO).

DTMSM was a colorless liquid of b.p. 70-72°C/0.2mmHg. The yield was
60% NMR spectra in CDCl₃: ¹H, δ 3.27ppm (s, 2H) and -0.24ppm (s, 18H); ¹³C, δ
166.96, 44.82 and -0.49ppm; and ²⁹Si (referenced to TMS in CDCl₃), δ 25.79ppm.

20 LiBMB was recrystallized from anhydrous acetone with a yield about 90%.
NMR spectra in DMSO-*d*₆: ¹H, δ 3.39ppm; ¹³C, δ 166.03 and 38.56ppm; ⁷Li
(referenced to LiNO₃ in D₂O), δ 1.04ppm; and ¹¹B (referenced to BF₃·Et₂O in CDCl₃),

δ 8.26ppm. Elemental analysis: found C 32.15%, H 2.11%, calculate (for $C_6H_4O_8BLi$) C 32.43%, H 1.80%.

Example 3

This example illustrates another way to synthesize the lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two malonyl groups, to give an anion of bis(malonato)borate, LiBMB. The preparation was similar to the second step in Example 1. 0.2 mol malonic acid, boric acid and 0.1 mol lithium hydroxide monohydrate were dissolved in some distilled water and boiled in an oil bath of around 130°C overnight to evaporate all water. The residual solid was further dried in a vacuum oven at 100°C for one day and then recrystallized in anhydrous acetone to give a white solid, which was dried in a vacuum oven at 100°C for 48 hours. The characterization results were the same as in Example 2.

Example 4

This example illustrates the synthesis of a lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two succinyl groups, to give an anion of bis(succinato)borate. This compound has a formula lithium bis(succinato)borate, LiBSB. The preparation includes three steps similar to those in Example 1, just using succinic acid to replace oxalic acid and di(trimethylsilyl) succinate (DTMSS) to replace di(trimethylsilyl) oxalate.

Example 5

This example illustrates another way to synthesize the lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two succinyl groups, to give an anion of bis(succinato)borate, LiBSB. The preparation was similar to that in Example 3, just using succinic acid to replace malonic acid.

Example 6

This example illustrates the synthesis of a lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by one malonyl group and one oxalyl group, to give an anion of malonato oxalato borate. This compound has a formula lithium (malonato oxalato) borate, LiMOB. The preparation included the similar steps in Example 1, just by stirring equal molar lithium tetramethanolatoborate, $\text{LiB}(\text{OCH}_3)_4$, di(trimethylsilyl) malonate (DTMSM) and mol di(trimethylsilyl) oxalate (DTMSO) in anhydrous acetonitrile at 45-50°C overnight. LiMOB was recrystallized from anhydrous acetonitrile with a yield about 86%. NMR spectra in $\text{DMSO}-d_6$: ^1H , δ 3.52ppm; ^{13}C , δ 165.56, 158.49 and 38.35ppm; ^7Li (referenced to LiNO_3 in D_2O), δ 0.99ppm; and ^{11}B (referenced to $\text{BF}_3 \cdot \text{Et}_2\text{O}$ in CDCl_3), δ 9.91ppm (integral 95.5%) and 12.03ppm (integral 4.5%), which indicated the presence of small amount of lithium bis(oxalato)borate, LiBOB, as an impurity in the product. LiBOB may be removed by the treatment of anhydrous tetrahydrofuran to give a pure LiMOB.

Example 7

This example illustrates another way to synthesize the lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by one malonyl group and one oxalyl group, to give an anion of malonato oxalato borate, LiMOB. The preparation was similar to that in Example 3, by boiling the aqueous solution of equal mol malonic acid, oxalic acid, boric acid and lithium hydroxide monohydrate in an oil bath of around 130°C overnight to evaporate all water. The dried crude product was recrystallized in anhydrous acetonitrile to give white solid which was

then dried in a vacuum oven at 100°C for 48 hours. The characterization results were the same as in Example 5.

Example 8

This example illustrates the synthesis of a lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two methylenedisulfonyl groups, to give an anion of bis(methylenedisulfonato)borate. This compound has a formula lithium bis(methylenedisulfonato)borate. The preparation includes the similar three steps in Example 2, but using methylenedisulfonic acid to replace oxalic acid and di(trimethylsilyl) methylenedisulfonate to replace di(trimethylsilyl) oxalate.

10 Example 9

This example illustrates a method to synthesize the lithium salt of an orthoborate in which the four boron oxygens are pairwise connected by two sulfoacetyl groups, to give an anion of bis(sulfoacetato)borate. This compound has a formula lithium bis(sulfoacetato)borate. The preparation was similar to the second step in Example 4, but using sulfoacetic acid to replace malonic acid.

Example 10

This example illustrates the preparation of electrolytic solutions of lithium orthoborate salts, chosen from any of the salts presented hereinabove, in non-aqueous solvents. The non-aqueous solvent is chosen from carbonate, non-carbonate plasticizers or their mixtures. Suitable carbonate plasticizers are, for example, ethylene carbonate (EC), propylene carbonate (PC), butylene carbonate (BC), dimethyl carbonate (DMC) and diethyl carbonate (DEC). Suitable non-carbonate plasticizers are 1,2-dimethoxyethane (DME), 1,2-diethoxyethane (DEE), dimethylsulfoxide (DMSO), dimethyl sulfone (DMS), ethylmethylsulfone (EMS), γ -

butyrolactone (BL). Preferred plasticizer mixtures are EC-PC, EC-DMC, EC-DMC-DEC, and PC-DME.

In a dry glove box, a certain amount of lithium orthoborate salt was placed into a volumetric flask and the non-aqueous solvents or solvent mixtures were added.

- 5 The mixture was shaken occasionally to allow all salt to dissolve and the solution mixing well. The conductivity data of some of these solutions are given in Figures 2 to 4.

Example 11

- This example illustrates the preparation of a gel electrolyte containing lithium
10 bis(oxalato)borate prepared in Example 1.

- In a dry glove box, the lithium salt from Example 2 was dissolved in a certain amount of EC-PC (1:1, o/w) mixture in a vial. A quantity poly(methyl methacrylate), PMMA, with high molecular weight of 996,000 was added. The vial was sealed and heated to around 140°C with occasionally shaking till the mixture was well done. The
15 hot viscous mass was pressed in between two stainless steel plates covered with Teflon films. After cooling, the self-standing membrane was peeled off. The conductivity of the gel electrolyte is given in Figure 5.

Example 12

- This example illustrates the electrochemical properties of an electrolytic
20 solution of lithium orthoborate salt from Example 8. The cyclic voltammograms were measured at room temperature on an EG&G potentiostat/galvanostat model 273, with a three-electrode dip-cell with platinum, stainless steel, nickel, aluminum or copper wire as working electrode and lithium metal as counter and reference electrodes. The scan rate was 1 mVs⁻¹. The cyclic voltammetric results are given in Figures 6 to 8.

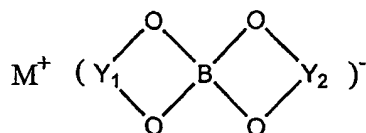
Example 13

This example illustrates the battery performance of an electrolytic solution of lithium orthoborate salt from Example 10. Prototype lithium rechargeable batteries were assembled by pressing into appropriate cases a sequence of a lithium metal disk
5 anode, a glass fiber film saturated with an electrolytic solution of lithium orthoborate salt from Example 10, and a composite cathode membrane. The latter was a blend of $\text{LiCr}_{0.015}\text{Mn}_{1.985}\text{O}_4$ as the active intercalation material, carbon black as an electronic conductor and PVdF as a polymer binder, in a weight ratio of 82:10:8. The batteries were assembled in a VAC dry box filled with purified argon. Preliminary
10 investigation into the battery characteristics and performance was performed by examining their galvanostatic charge-discharge cyclic curves.

Those skilled in the art will appreciate that numerous changes and modifications may be made to the preferred embodiments of the invention and that such changes and modifications may be made without departing from the spirit of the
15 invention. It is therefore intended that the appended claims cover all such equivalent variations as fall within the true spirit and scope of the invention.

We claim:

1. Electrolytic salts having the formula



2

3

wherein:

B is boron;

O is oxygen;

Y_1 and Y_2 are each bound to a pair of said oxygens and are selected from the

group comprising $XC-(CR_2)_aCX$ wherein a is 0 to 4 and X is $=O$, $-C=N$, CR'_3 or R'_3

wherein R' is halo, R is hydrogen, alkyl, cyano, or halo provided that when a is 0 and

X is CF_3 or $=O$, Y_1 is not Y_2 , and $O_2S(CR_2)_bSO_2$ and $OC(CR_2)_bSO_2$ wherein b is 1 to

4 and R is hydrogen, alkyl, or halo, wherein Y_1 and Y_2 are the same or different in

each occurrence; and

M^+ is a metal ion selected from the Group I or Group II elements.

2. An electrolytic salt of Claim 1 having the formula lithium

bis(malonato)borate.

3. An electrolytic salt of Claim 1 having the formula lithium

bis(succinato)borate.

4. An electrolytic of Claim 1 having the lithium (malonato oxalato borate).

5. An electrolytic salt of Claim 1 having the formula

bis(methylenedisulfonato)borate.

1 6. An electrolytic salt of Claim 1 having the formula
2 bis(methylenedisulfonato)borate.

1 7. An electrolytic salt of Claim 1 having the formula lithium
2 bis(sulfoacetato)borate.

1 8. An electrolytic salt of Claim 1 having the formula selected from the group
2 comprising lithium bis(hexafluoropropylenediolato)borate and 1,2-
3 tetra(trifluoromethyl)ethylenediolato(2-)O,O'.

1 9. A method of making a compound of Claim 1 comprising providing a
2 fluoro-substituted diol or dibasic acid form of said Y₁ and Y₂, and combining said
3 fluoro-substituted diol or dibasic acid form with M hydroxide and boric acid under
4 conditions whereby Y₁ and Y₂ bind pairwise to oxygens in said anion.

1 10. Electrolytic salts produced by the method of Claim 9.

1 11. A method of making an electrolytic salt of Claim 1 comprising providing:

- 2 a. di(methylsilyl)Y₁ and di(methylsilyl)Y₂; and
3 b. alkoxy orthoborate salt; and
4 c. combining said di(methylsilyl)Y₁, said di(methylsilyl)Y₂; and
5 said alkoxy orthoborate salt under conditions whereby said electrolytic salt is formed.

1 12. The method of Claim 11 wherein said alkoxy orthoborate salt is lithium
2 tetramethanolatoborate.

1 13. Electrolytic salts made by the method of Claim 11.

1 14. The electrolytic salt lithium bis (oxalato borate) produced by the method of
2 Claim 11.

1 15. An electrolytic salt of Claim 1 in a non-aqueous solvent.

1 16. An electrolytic salt of Claim 15 wherein said solvent is selected from the
2 group comprising ethylene carbonate, propylene carbonate, butylene carbonate,

3 dimethyl carbonate ,diethyl carbonate 1,2-dimethoxyethane ,1,2-diethoxyethane ,
4 dimethylsulfoxide and dimethyl sulfone (DMS), ethylmethysulfone (EMS), γ -
5 butyrolactone or mixtures thereof.

1 17. The electrolytic salt lithium bis (oxalato borate) in a non-aqueous solvent
2 wherein said solvent is selected from the group comprising ethylene carbonate ,
3 propylene carbonate, butylene carbonate , dimethyl carbonate ,diethyl carbonate 1,2-
4 dimethoxyethane ,1,2-diethoxyethane , dimethylsulfoxide, dimethyl sulfone (DMS),
5 ethylmethysulfone (EMS), γ -butyrolactone or mixtures thereof.

1 18. A conductive polymeric gel comprising an electrolyte of Claim 1.

1 19. A conductive polymeric gel comprising lithium bis (oxalato borate).

1 20. An electrolytic salt of Claim 1 in a lithium battery.

1 21. A conductive electrolytic salt of Claim 15 in a lithium battery.

1 22. A conductive polymeric gel of Claim 18 in a lithium battery.

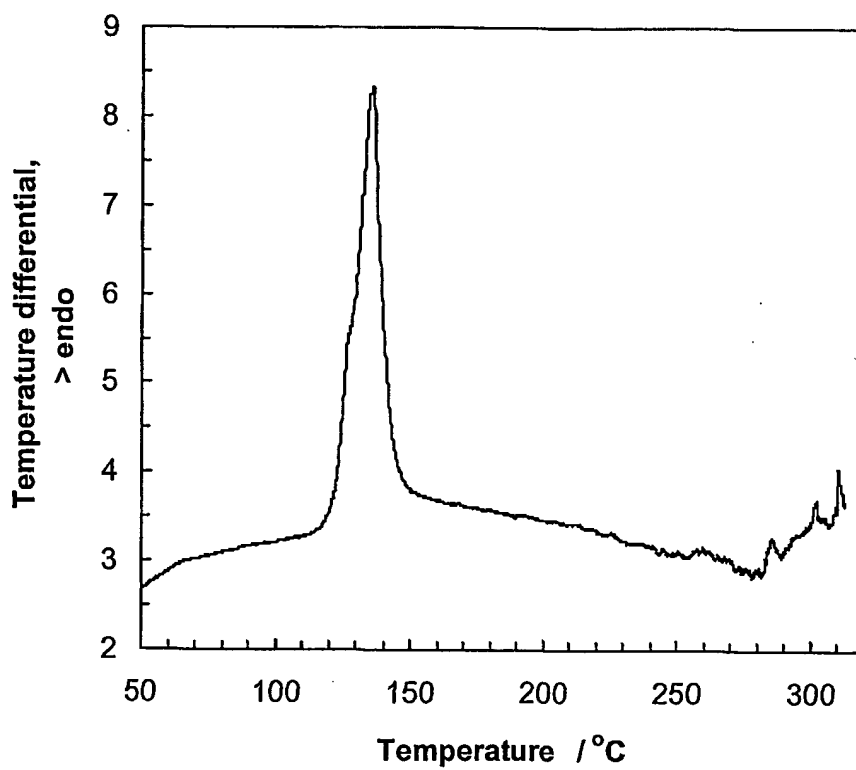


Figure 1. DTA trace thermogram at $10^{\circ}\text{C min}^{-1}$ for pure $\text{LiB}[\text{OC}(\text{CF}_3)_2]_4$ or LiBPFPB, showing fusion at 120°C and decomposition at 280°C .

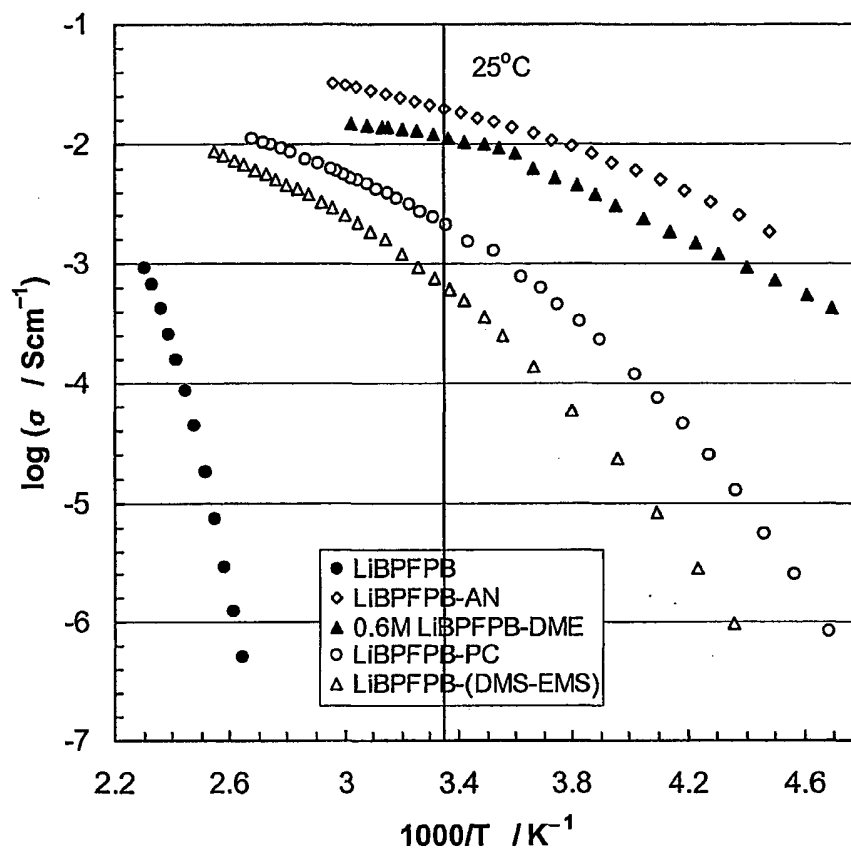


Figure 2. Ionic conductivities of LiBPFb and its solutions in 1M acetonitrile (AN), 0.6M DME, 1M PC and 1M DMS-EMS (15:85 by weight).

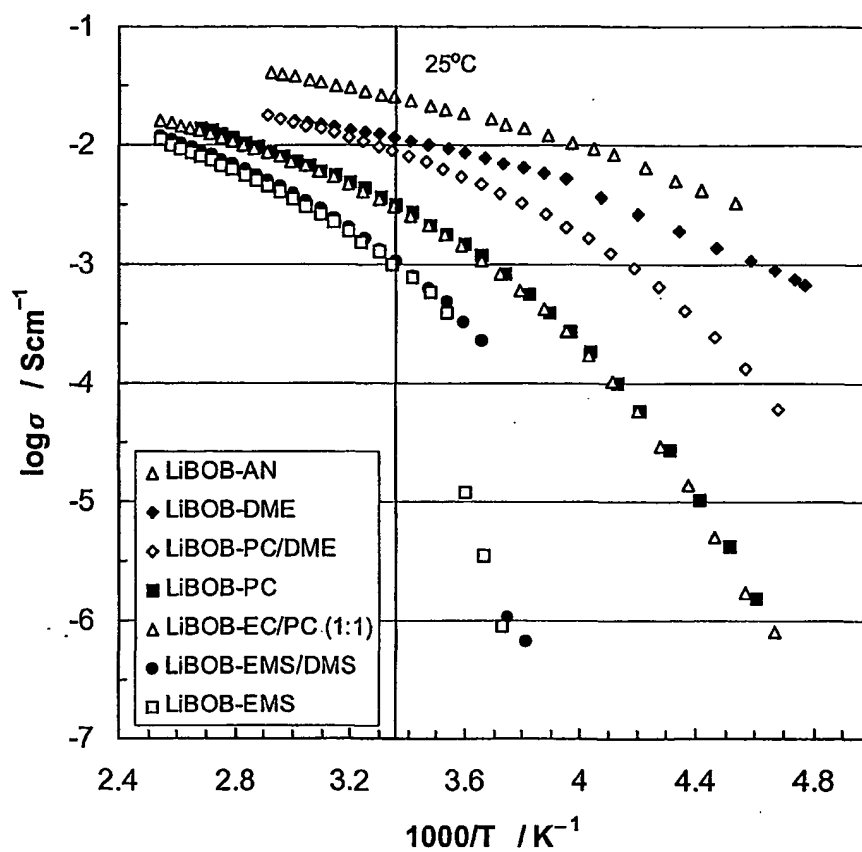


Figure 3. Ionic conductivities of 1M LiBOB solutions.

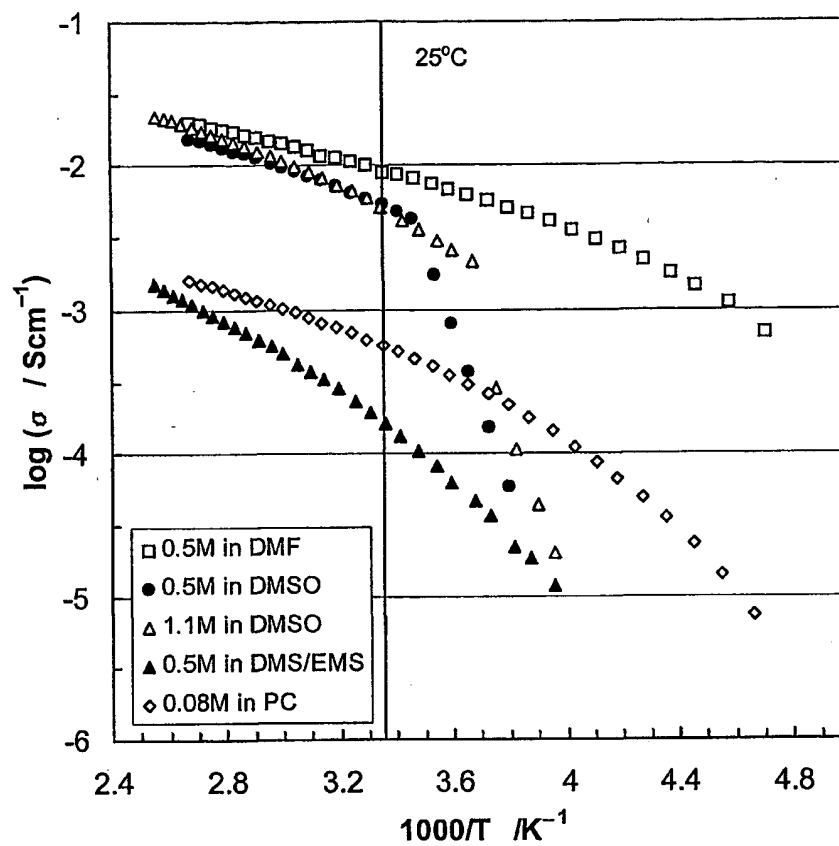


Figure 4. Ionic conductivities of LiBMB solutions.

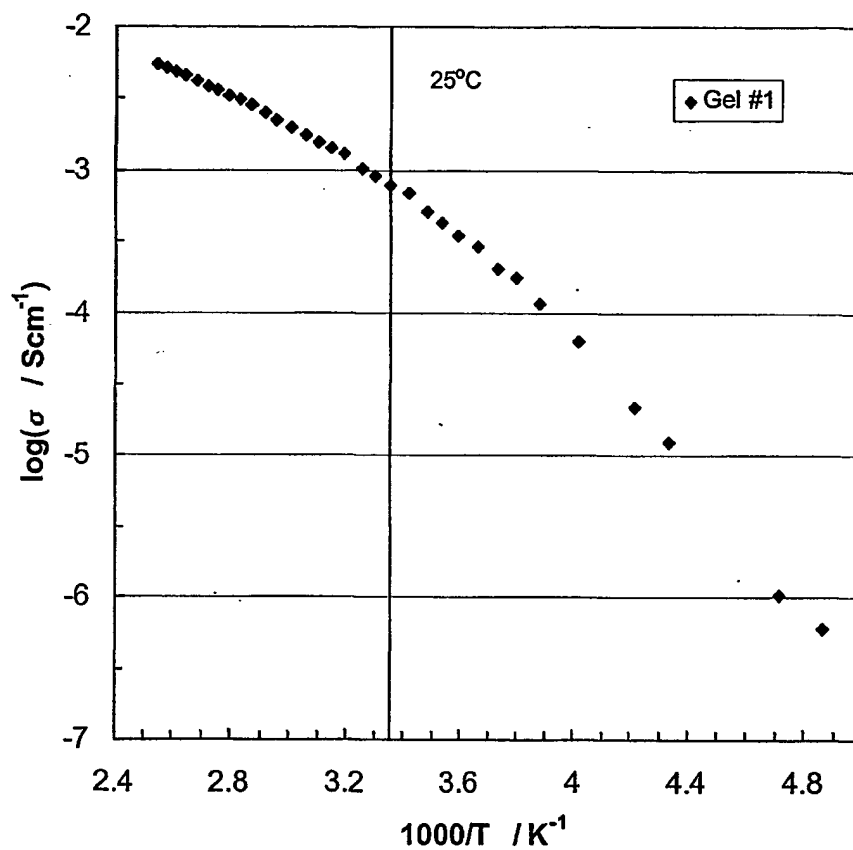


Figure 5. Temperature dependence of ionic conductivity of a gel electrolyte (Gel #1) with composition of 21.17 PMMA (MW 996,000), 7.88 LiBOB, 35.48 EC and 35.47 PC.

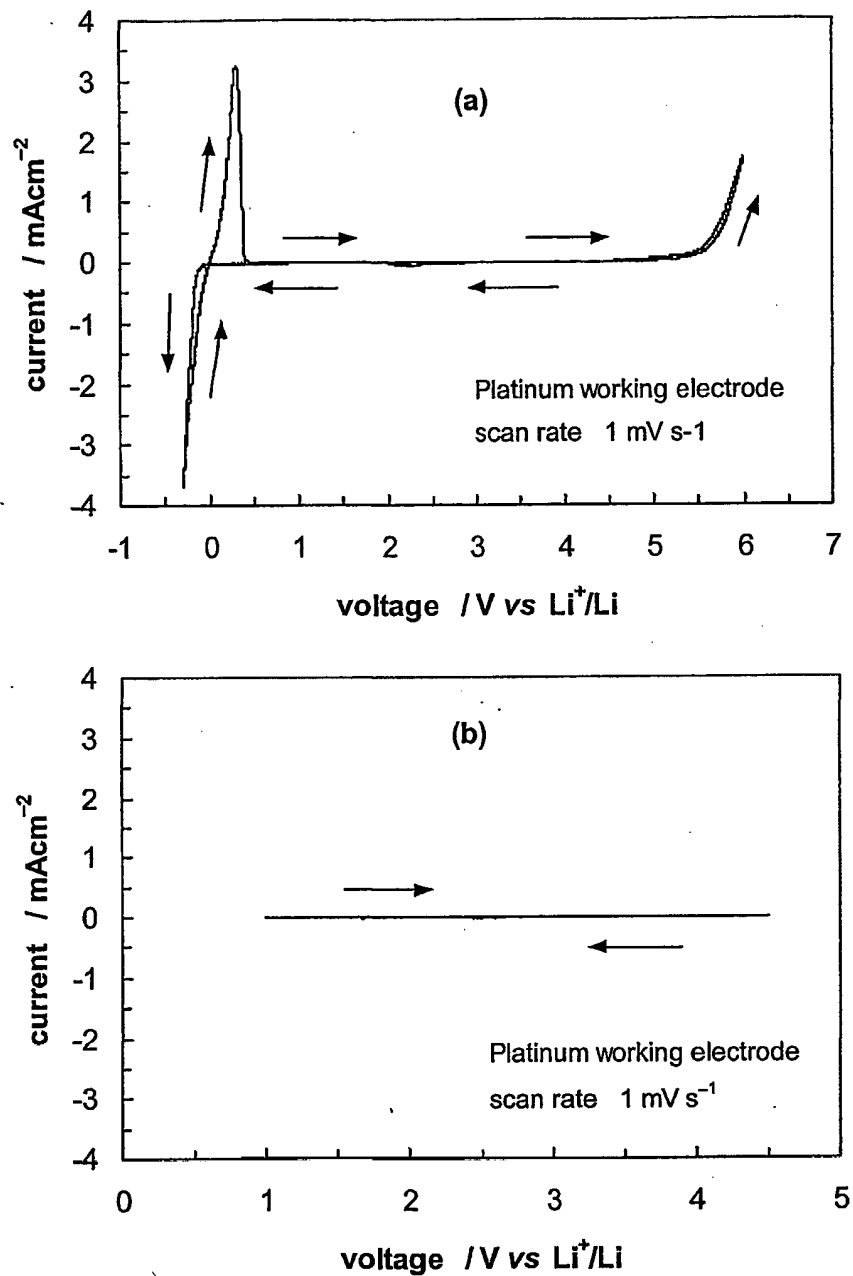


Figure 7. Lithium deposition-stripping process and electrochemical stability of 1M LiBOB-PC solution scanned at 1 mV s^{-1} in the voltage range of (a) $-0.3 \sim 6$ V and (b) $1 \sim 4.5$ V vs. Li^+/Li at room temperature. The area of platinum wire working electrode is $4.91 \times 10^{-4} \text{ cm}^2$. The "window" is at least 4.5 V.

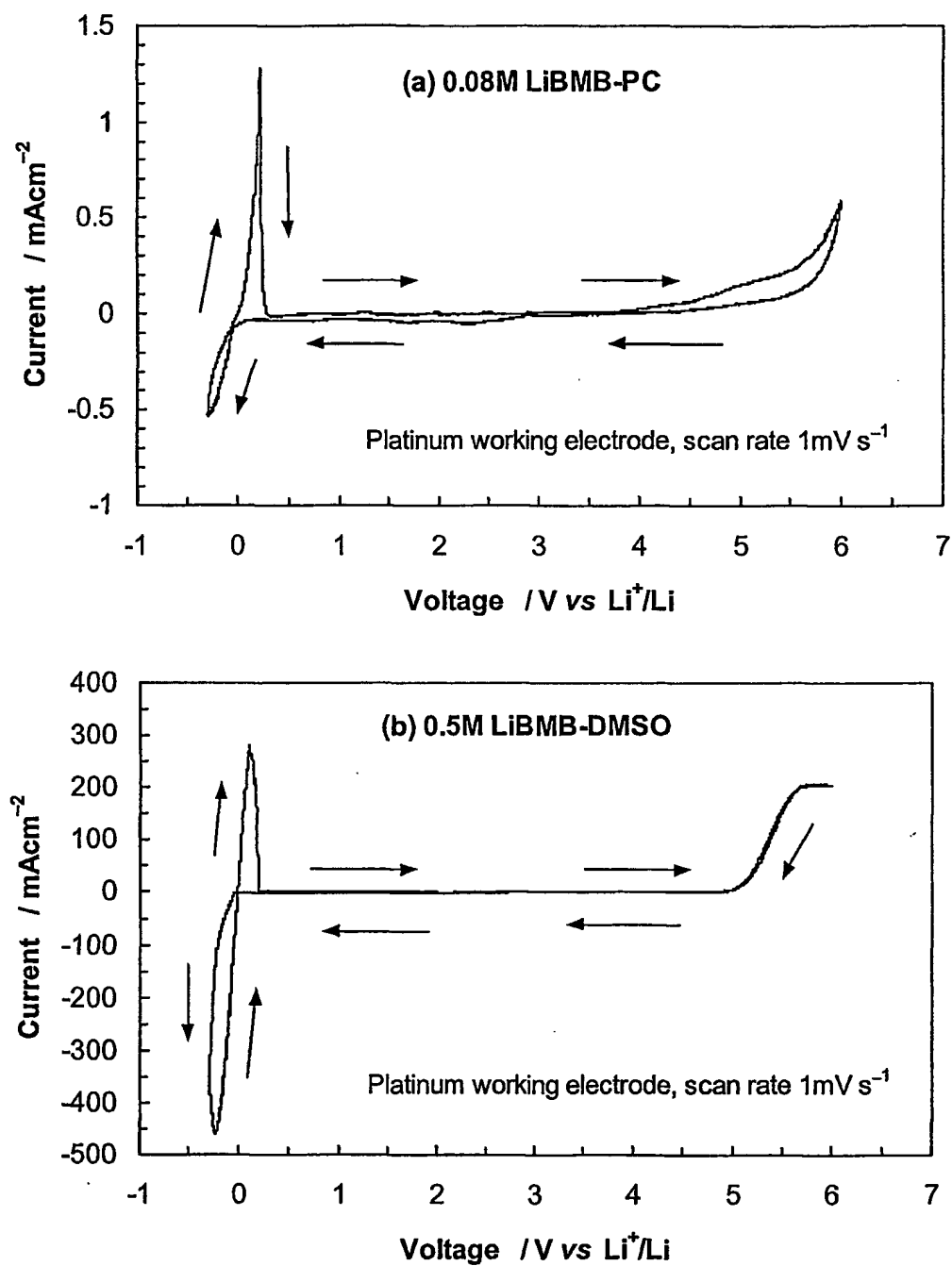


Figure 8. Electrochemical stability of LiBMB solutions in PC (a) and DMSO (b), respectively. Area of platinum working electrode $4.91 \times 10^{-4} \text{ cm}^2$.

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